sometimes co-occurs with deoxynivalenol. Zearalenone can be extracted from grain with chloroform and cleaned up using a silica gel column, followed by defatting by partitioning between hexane and acetonitrile. For TLC the samples and standards are dissolved in benzene and spotted on a silica gel and developed with ethanol–chloroform (5 : 95 v/v) or acetic acid–benzene (5 : 95 v/v). Under 254 nm ultraviolet light, zearalenone appears as a greenish-blue fluorescent spot at $R_F = 0.5$. If the plate is sprayed with an aluminium chloride solution and heated for 5 min at 130°C, zearalenone will appear under 365 nm ultraviolet light as a blue fluorescent spot.

Summary

TLC methods have been developed to analyse for a variety of mycotoxins in the commodities in which they occur. TLC densitometric determinations provide precise quantitative data at ng g^{-1} to μg g^{-1} levels. The major advantages of TLC over LC are its low cost and its use as a screening tool. The commercial availability of precoated TLC plates, including silica gel, reversed-phase and high performance plates has resulted in expanded applications in the mycotoxin field. The role of TLC in the analysis of mycotoxins will continue for the foreseeable future.

See also: **II/Chromatography: Thin-Layer (Planar):** Historical Development; Preparative Thin-Layer (Planar) Chromatography. **III/Aflatoxins and Mycotoxins:** Chromatography. **Immunoaffinity Extraction.**

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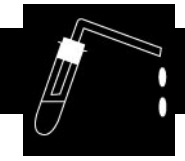
AIR LIQUEFACTION: DISTILLATION



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Oxygen, nitrogen and argon, the major components of air, have been separated by distillation at cryogenic temperatures for nearly a century. Air was commercially liquefied as early as 1895 by Carl von Linde and also by William Hampson. Linde separated oxygen from air by distillation in a single column in 1902. A commercial plant producing pure nitrogen was already in operation by 1904. The first double-column distillation system, the predecessor to current double-column processes, was commissioned in 1910 by Linde. Argon was produced on an industrial scale by 1913. Today the major industrial companies supplying products from air distillation and liquefaction and also the equipment for this purpose are: AGA, Air Liquide, Air Products and Chemicals, the BOC Group, Linde, Messer Group, Nippon Sanso and Praxair.

The composition of dry and impurities-free air is given in **Table 1**. The critical temperature and normal boiling point (at 101.3 kPa) for each component is also listed. In this table, and in the rest of this chapter, concentration in p.p.m. refers to parts per million on a volume basis. The gases listed in Table 1 are used in

Table 1 Composition of air and thermodynamic properties of its constituent gases

Constituent gas	*Concentration (mol%)*	*Boiling temperature (°C)*[a]	*Critical temperature (°C)*
Nitrogen	78.12	− 195.8	− 146.9
Oxygen	20.95	− 182.9	− 118.8
Argon	0.93	− 185.9	− 122.4
Neon	18 p.p.m.	− 246.1	− 228.8
Helium	5.3 p.p.m.	− 268.9	− 267.9
Krypton	1.1 p.p.m.	− 153.4	− 63.8
Xenon	0.08 p.p.m.	− 108.1	− 16.6

[a] Boiling temperature at 101.3 kPa.

a wide range of industrial and medical applications. Typical industries using these gases include: ferrous and nonferrous metals, chemicals, petroleum, food, paper, glass, textile and electronics. Oxygen is generally used as an oxidant while nitrogen and argon are used to provide inert atmospheres. Krypton is used in light bulbs, lasers, sputtering of electronic components and high energy physics. Neon is used in fluorescent lighting, infrared detection equipment and experimental physics at cryogenic temperatures. Xenon is used in electronic flashlights, as an anaesthetic and in a new application where an on-board xenon ion propulsion system is used for positioning a satellite. Helium is not generally recovered from air due to its low concentration.

The history of air distillation started with oxygen production followed by recovery of other constituents. Therefore, the distillation processes to produce oxygen are described first here followed by argon and then nitrogen. These topics are followed by liquefaction processes and finally a brief description is given of the major equipment used in cryogenic air separation and liquefaction processes.

Distillation

Distillation of Air to Recover Oxygen

The basic steps of any cryogenic air distillation process are shown in **Figure 1**.

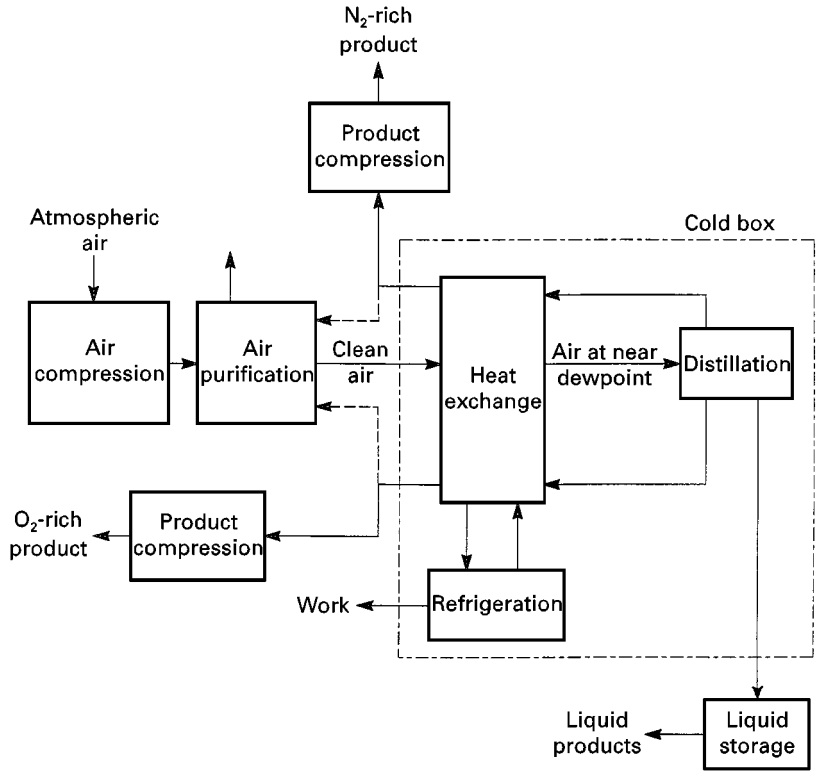

Figure 1 Basic steps in a cryogenic air distillation plant.

Air is first compressed in a multistage compressor and cooled to near ambient temperature. Given the boiling point temperatures of nitrogen and oxygen in Table 1, it is clear that air has to be cooled to extremely low temperatures before it can be distilled. It follows that a number of impurities present in air and which would freeze at such cryogenic temperatures must be removed to avoid plugging of heat exchange and separation equipment. Typical impurities that are not listed in Table 1 but are present in air include: water (after compression air is saturated); carbon dioxide (about 375 p.p.m.); hydrocarbons such as acetylene (0.1–1 p.p.m.), methane (2–10 p.p.m.) and some higher hydrocarbons in varying concentrations (ethylene, propylene, ethane, etc.); carbon monoxide; nitrogen oxides and sulfur compounds. Therefore, in the second step, compressed air is sent through a purification system at least to remove impurities such as water, carbon dioxide, acetylene, nitrogen oxides and sulfur compounds.

In the third step, the compressed and cleaned air is cooled to near its dewpoint by heat exchange. Finally, the cooled air is sent to an appropriate distillation column system. Here air is distilled into at least two product steams – one stream is enriched in oxygen and the other is enriched in nitrogen. Both of these streams are then warmed to near ambient temperature by countercurrent heat exchange with the incoming air. When a product stream is required at a higher pressure, it is further compressed. Liquid products such as liquid oxygen, liquid nitrogen or liquid argon can also be produced from the distillation column system and sent to liquid storage for later distribution.

The heat exchanger and the distillation system are enclosed in a well-insulated enclosure called the cold box. Despite the insulation, there is heat leakage and therefore, refrigeration is provided to the cold box to keep the inside equipment cold. For this purpose, modern cryogenic plants employ turbo-expanders that are also enclosed in the cold box. These turbo-expanders produce work out of the cold box and keep all the equipment at the desired cryogenic temperatures.

Now that the basic steps that are common to all the air distillation plants have been described, attention will be paid to the distillation of air after it is cooled to near its dewpoint temperature. The distillation of air is at the heart of an air separation plant and its arrangement varies with the number, quantity and purity of products being produced.

The early developments in air distillation to produce oxygen were propelled by the invention of the oxyacetylene blow torch for welding and steel cutting. In 1902, Carl von Linde introduced the first air distillation process using a single distillation column. A simplified sketch of this single column arrangement is shown in **Figure 2**.

Compressed, cleaned and cooled air that is near its dewpoint temperature is first condensed in a reboiler-condenser located in the bottom (sump) of the distillation column. The condensed liquid air is then reduced in pressure across a valve and fed to the top of the distillation column. The stream provides both the feed and the liquid reflux. From Table 1 it can be seen that, of the three major components in air, nitrogen is the most volatile, oxygen the least volatile and argon is of intermediate volatility. As a result, the liquid descending the distillation column becomes enriched in oxygen. The vapour needed for distillation is provided by boiling the oxygen-enriched liquid in the sump by heat exchange against the condensing air in the reboiler-condenser. A portion of the vapour rising from the sump is collected as gaseous oxygen product while the rest is allowed to travel up the distillation column. As vapour ascends the distillation column, it becomes enriched in nitrogen and finally leaves from the top of the column as a nitrogen-enriched waste stream. If needed, a liquid oxygen product stream is collected from the sump of the distillation column. Even when liquid oxygen is not a desired product, a very small quantity of liquid oxygen is continuously withdrawn from the bottom of the distillation column to avoid accumulation of hydrocarbons in the sump. Both the gaseous oxygen product stream and nitrogen-rich vapour stream are then warmed to near

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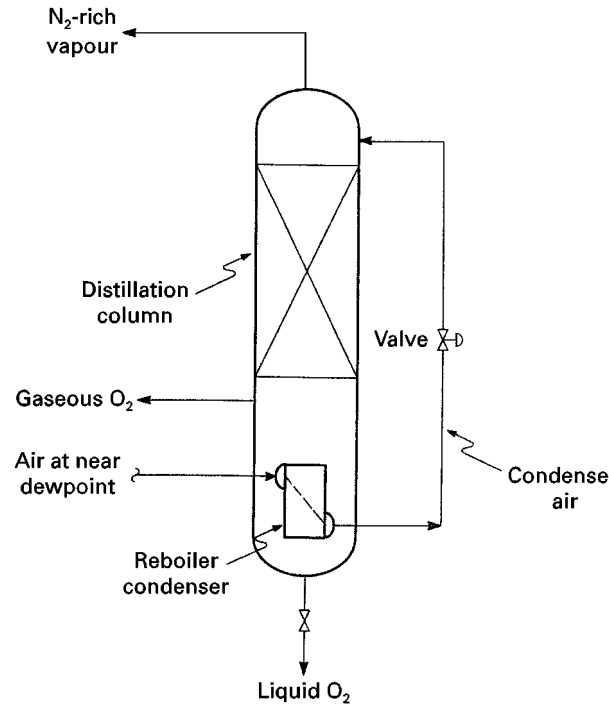

Figure 2 A single column to produce oxygen.

ambient temperature by heat exchange against the incoming air stream (**Figure 1**). While the early plants produced oxygen at a purity of 80–90%, the single-column process can provide oxygen at any desired higher purity. Generally, the purity of oxygen used in metal welding and cutting is 99.5% or greater.

The problem with the single distillation column process shown in **Figure 2** is that the recovery of oxygen is low. The reason is that the minimum concentration of oxygen in the nitrogen-rich vapour stream leaving the top of the distillation column is limited to that value which is in equilibrium with the liquid air that is fed at the top. Since the concentration of oxygen in air is fairly high, a sizeable fraction of the oxygen in the feed air leaves in the nitrogen-rich vapour stream. To illustrate this for a distillation column operating at 1.4 atm and producing 99.5% oxygen, the pressure of feed air is about 5 atm and a vapour stream in thermodynamic equilibrium with the liquid air stream (at 1.4 atm) will be 6.9% oxygen. A typical oxygen recovery from such a distillation column would only be in the neighbourhood of 14 mol of oxygen per 100 mol of feed air.

It is clear that, for higher recoveries of oxygen, the concentration of oxygen in the nitrogen-rich vapour stream leaving the top of the distillation column must be low. In other words, both product streams should be relatively pure. This requires that the liquid reflux to the top of the distillation column should also be relatively pure. It seems that Georges Claude was the first to provide the solution by using his dephlegmation equipment in 1903. However, it was Carl von Linde's double distillation column of 1910 that revolutionized the industry and is still the workhorse of the modern cryogenic oxygen plants.

A typical double distillation column configuration is shown in **Figure 3**.

In this arrangement, compressed, cleaned and cooled air is now sent to a high pressure distillation column that operates at about 6 atm. As the vapour rises up this high pressure column, it is enriched in nitrogen and at the top of the column, the concentration of oxygen has been reduced to an extremely low level. The nitrogen vapour is condensed by heat exchange in a reboiler-condenser. Of this condensed nitrogen stream, about 60% is returned back to the top of the high pressure column as liquid reflux; approximately 40% of the flow is sent to the top of a low pressure column that operates at around 1.4 atm. The liquid descending the high pressure column becomes enriched in oxygen to produce crude liquid oxygen leaving the bottom (typically around 35% oxygen). This crude liquid oxygen is reduced in pressure across a valve and fed to an intermediate location in the low pressure column. In the low pressure column, crude liquid oxygen is distilled to produce a nitrogen-rich vapour stream at the top and an oxygen product stream at the bottom. The boil-up at the bottom of the low pressure column is provided by vaporizing the liquid oxygen stream in the sump by heat exchange against the condensing nitrogen vapour stream from the top of the high pressure column. A portion of the vapour from the reboiler-condenser is recovered as gaseous oxygen product while the rest rises to perform distillation in the low pressure column. When needed, some liquid oxygen can also be recovered from the sump as product.

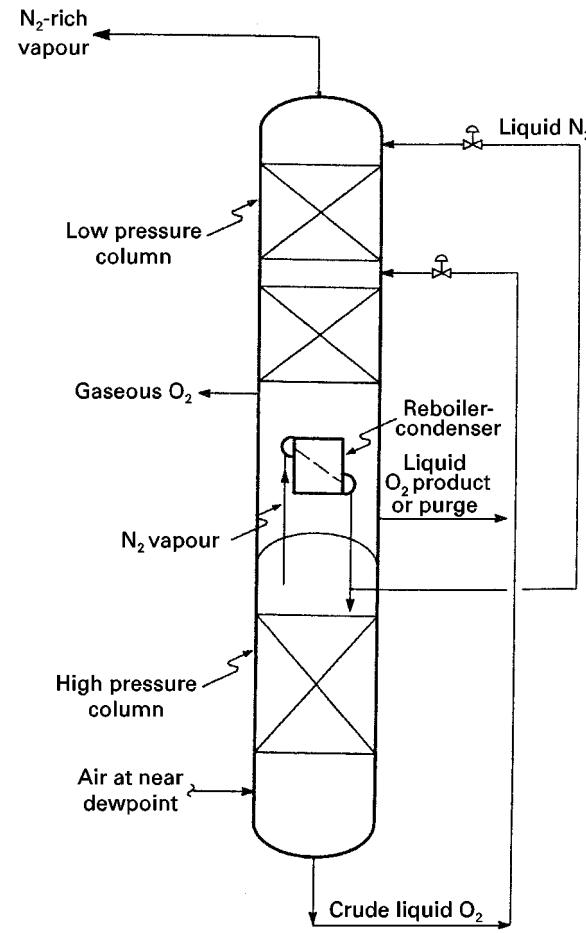

Figure 3 A double-column arrangement to produce oxygen.

In a double-column arrangement, the main purpose of the high pressure column is to distil and provide two saturated liquid streams from the feed air – a liquid nitrogen reflux and a crude liquid oxygen feed. It is in the low pressure column that the crude liquid oxygen is distilled to provide the needed oxygen product stream. The liquid nitrogen stream provides the much needed liquid reflux at the top of the low pressure column. By using sufficient stages of separation in the high pressure column, the concentration of oxygen in the liquid nitrogen stream can

often be reduced to p.p.m. level. Therefore, the concentration of oxygen in the nitrogen-rich vapour stream from the top of the low pressure column is reduced to extremely low levels. This not only allows the potential to recover the nitrogen-rich vapour stream as a useful product stream, but also makes very high recoveries of oxygen possible. For a double-column process, production of 99.5% oxygen in excess of 20.5 mol per 100 mol of feed air (maximum oxygen content being 20.95 mol) is quite common.

For most uses, gaseous oxygen is needed at pressures greater than atmospheric pressure. This pressure can range from about 2 atm absolute pressure for glass-making to pressures in the range of 30–80 atm for the gasification of hydrocarbons such as coal and petroleum residuum. One obvious method to deliver pressurized oxygen is to compress gaseous oxygen to the desired pressure after it exits the cold box. However, safety considerations tend to make the equipment associated with oxygen compressors expensive. In certain applications, where both oxygen and nitrogen are needed at higher pressures, one has the option of increasing the pressure of the distillation columns and directly produce both products at elevated pressures. Unfortunately, the low pressure column is seldom operated at pressures greater than 8 atm absolute. This is because the pressure of the high pressure column is typically greater than two to three times the pressure of the low pressure column and distillation in the high pressure column must be conducted at a pressure that is sufficiently lower than the critical pressures of nitrogen and oxygen. A third method that is becoming more popular is the use of a pumped liquid oxygen process. This method is also sometimes referred as internal oxygen compression. A schematic of such a plant is shown in **Figure 4**.

In the pumped liquid oxygen process of Figure 4, air is compressed in a multistage air compressor (MAC) to about 6 atm absolute pressure, cooled to near ambient temperature and then sent to a molecular sieve purifier. About 70% of the cleaned air is directly fed to the cold box for cooling in the main heat exchanger. From an intermediate location of the main heat exchanger, corresponding to 100°C to −130°C, approximately 10–20% of this flow is withdrawn and expanded in a turbo-expander to a pressure slightly above atmospheric pressure and fed to an intermediate location of the low pressure column. The work extracted from the turbo-expander provides the needed refrigeration for the cold box. The air that remains after the withdrawal of expander feed is cooled to near the dewpoint temperature and is fed to the bottom of the high pressure column. The arrangement of the double distillation column process is the same as discussed in **Figure 3**, with only two differences. The first is that the liquid nitrogen stream from the top of the high pressure column is cooled in a subcooler heat exchanger against the nitrogen-rich vapour streams.

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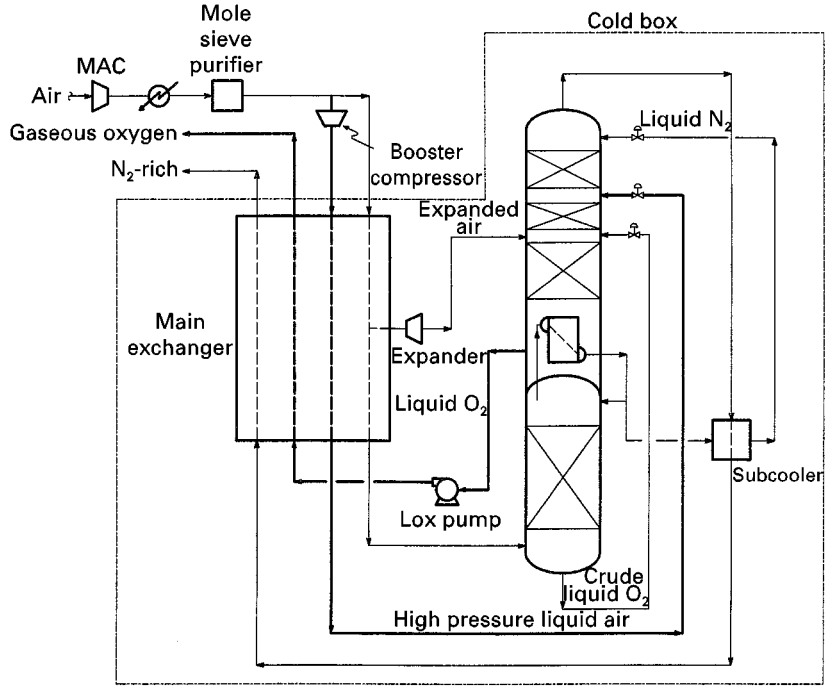

Figure 4 Pumped liquid oxygen flowsheet.

This increases the fraction of liquid in this stream as its pressure is reduced to that of the low pressure column. This technique, which is commonly used in any oxygen plant to increase liquid nitrogen reflux to the low pressure column, has the beneficial effect of increasing the purity and recovery of products.

The second major difference is the withdrawal of oxygen product from the low pressure column as liquid and its subsequent vaporization. The liquid oxygen is pumped in a liquid oxygen pump to the desired oxygen product pressure. This pumped liquid oxygen is then vaporized in the main heat exchanger. In order to maintain refrigeration balance, it is essential that another stream be condensed through heat exchange as the pumped liquid oxygen is being vaporized. For this purpose, about 30% of the cleaned air is further boosted to a higher pressure in a booster compressor. The pressure of the boosted air is chosen such that it would easily condense through heat exchange with the vaporizing oxygen stream. Generally the pressure of the condensing air stream is much greater than the oxygen stream. The condensed liquid air from the main heat exchanger is appropriately fed to either one or both of the distillation columns. The warmed gaseous oxygen stream provides the desired pressurized oxygen product.

While the early oxygen plants produced only a few tons of oxygen per day, modern plants are capable of producing in excess of 3000 tons per day of oxygen in a single train.

Distillation of Air to Recover Argon

After nitrogen and oxygen, argon is the most abundant component in air. Its inert property is quite attractive for metals and several other material-processing applications. Within a very short time of the discovery of the double-column system, argon was distilled from air in 1913. The distillation arrangement to produce argon in modern plants was generally described in a German patent by 1935.

The arrangement for argon production starts with an examination of the argon concentration profile in the low pressure column of a double-column process. From the normal boiling temperatures listed in **Table 1**, it is readily observed that the volatility of argon is between that of nitrogen and oxygen and, furthermore, it is closer to oxygen than nitrogen. As a result, the concentration of argon in the liquid nitrogen stream from the high pressure column (Figures 3 and 4) is at p.p.m. level and virtually all the argon is contained in the crude liquid oxygen. Therefore, the bulk of the argon in air enters at an intermediate point on the low pressure column. When oxygen containing less than 0.5% argon is produced, argon is forced to escape from the top of the low pressure column in the nitrogen-rich vapour stream. However, the liquid nitrogen reflux stream is virtually free of argon and tends to drive argon down the low pressure column. Consequently, the concentration of argon in the vapour phase at an intermediate location between the crude LOX feed and the oxygen product withdrawal point reaches levels approaching 20%. A typical vapour-phase argon concentration profile in the low pressure column is shown in **Figure 5**. The build-up of argon provides an opportunity to withdraw a side vapour stream from near the location where a peak in argon concentration occurs and to distil it further in a side distillation column to produce concentrated argon.

A typical argon recovery arrangement is shown in **Figure 6**. An argon-rich vapour stream containing between 10 and 25% argon, p.p.m. levels of nitrogen and the rest oxygen is withdrawn from an intermediate location of the bottom section of the low pressure column and is fed to the bottom of a side argon column. The flow of this vapour stream is about 20% of the feed air. As vapour ascends the side argon column, it is depleted in oxygen. The development of structured packing for cryogenic distillation columns has allowed the modern cryogenic plants to use in excess of 175 theoretical stages of separation in the side argon column. As a result, the vapour at the top of this column can contain only p.p.m. levels of oxygen. This vapour stream is condensed in a reboiler-condenser; most of it is returned back as reflux to the side argon column and a small portion is recovered as a crude argon stream. The liquid to vapour flow ratio in this column is in the neighbourhood of 0.97. The liquid from the bottom of the side argon column is

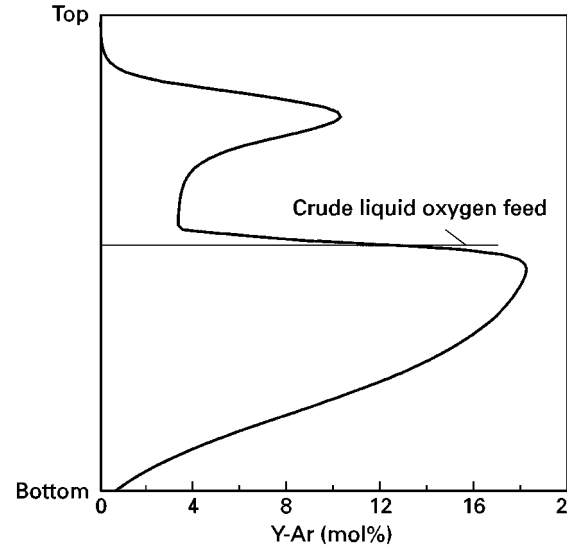

Figure 5 Vapour-phase composition in the low pressure column.

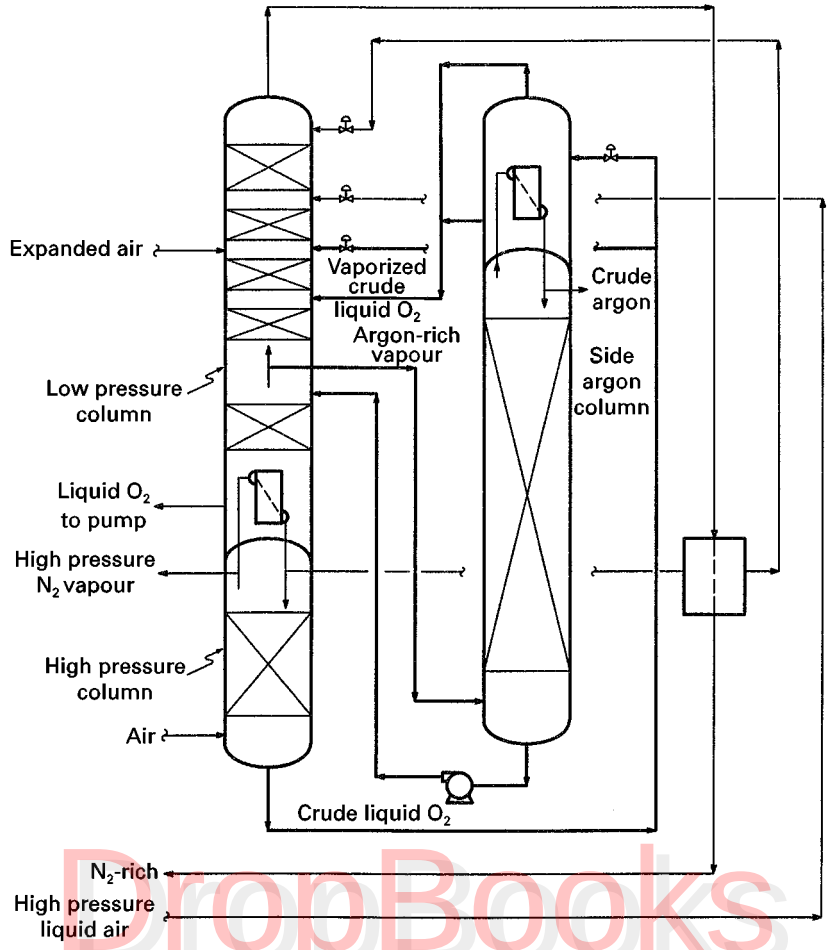

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Figure 6 Distillation arrangement for argon separation from air for the process shown in Figure 4.

pumped back to the argon-rich vapour draw location of the low pressure column. Condensation at the top of the side argon column is provided by boiling a portion of the crude liquid oxygen at nearly the low pressure column pressure, as shown in Figure 6. The vaporized crude liquid oxygen stream is fed to the low pressure column a few stages of separation below the location where the unboiled crude liquid oxygen is fed. The recovery of argon from cryogenic air is easily in the range of 70–85% and occasionally, if needed, it can be as high as 95% of the total argon contained in the feed air.

While the concentration of oxygen in the crude argon recovered from the arrangement in Figure 6 is below 5–100 p.p.m., the nitrogen concentration is much higher, as nearly all the nitrogen contained in the argon-rich vapour stream shows up in the crude argon. Generally, the argon product specification requires that the nitrogen concentration also be below 5 p.p.m. Therefore, the crude argon stream is subsequently distilled in a pure argon column with separation stages both below and above the feed. Boil-up and condensing duties for this column are extremely low and are easily provided by using side streams that are withdrawn from one or more appropriate process streams, shown in **Figure 6**, such as crude liquid oxygen, high pressure liquid air or high pressure nitrogen vapour. A waste vapour stream containing all the nitrogen is withdrawn from the top of the pure argon column and pure liquid argon product is collected and sent to a storage tank from the bottom of this column.

Distillation of Air to Recover Nitrogen

In most industrial applications, nitrogen is used as an inert gas. Cryogenic air separation can easily produce nitrogen gas with concentrations of oxygen below 5 p.p.m. Until the 1950s, the demand for nitrogen was low. Supply could easily be met by withdrawing a portion of nitrogen vapour from the top of the high pressure column as a co-product of a double-column process for oxygen production (for example, see Figure 6). Generally, up to 30% of the feed air can be recovered as high pressure nitrogen product from the top of the high pressure column. When needed, a portion of the nitrogen-rich vapour stream from the top

of the low pressure column can also be recovered as a useful product.

In the 1960s industrial demand for nitrogen increased, and this led to a need for plants that were designed solely for nitrogen with no co-production of oxygen. For most applications, nitrogen product is required at a pressure between 6 and 10 atm. There are two basic schemes for nitrogen separation from air: one uses a single column while the other uses two columns (similar to the double-column process for oxygen production). The single-column process is used for relatively small size nitrogen plants (up to about 500 tons per day of nitrogen) and two-column processes are used for larger size plants. Cold boxes can now be designed to produce as much as 10 000 tons per day of nitrogen in a single train.

A single-column process for nitrogen separation is shown in **Figure 7**.

Feed air is compressed to a pressure in excess of about 5 atm absolute, cleaned of impurities in the molecular sieve purifier and cooled to near its dew-point in the main heat exchanger by heat exchange against the returning streams. The cooled air stream is then fed to the bottom of a single column. Sufficient separation stages are used in this column to attain the desired purity at the top of this column. A portion of the nitrogen vapour from the top is withdrawn and warmed in the main heat exchanger to provide the desired nitrogen product. The rest of the nitrogen vapour stream is condensed in a reboiler-condenser and returned as reflux to the column. The ratio of liquid to vapour flow rates in the column is in the neighbourhood of 0.6. The crude liquid oxygen stream from the bottom of the column is reduced in pressure and vaporized in the reboiler-condenser. The vaporized stream is partially warmed in the main heat exchanger and then expanded in a turbo-expander to near atmospheric pressure to provide the needed refrigeration for the plant. The expanded stream is then warmed to near ambient temperature in the main heat exchanger and eventually discharged as an oxygen-rich waste stream. The concentration of oxygen in the waste stream is approximately 35%. The flow rate of the nitrogen product stream is about 40–50 mol per 100 mol of the feed air.

The main problem with the single-column process is that the crude liquid oxygen leaving from the bottom of the column is at best, in thermodynamic equilibrium with the feed air. This means that there is a lower limit to the concentration of nitrogen in the crude liquid oxygen stream. This limits the recovery of nitrogen. For higher recoveries of nitrogen and more efficient processes, it is essential that the crude liquid oxygen stream be further distilled to recover the contained nitrogen. **Figure 8** shows such a two-column process.

The major difference between this process and the single-column process of **Figure 7** is that now

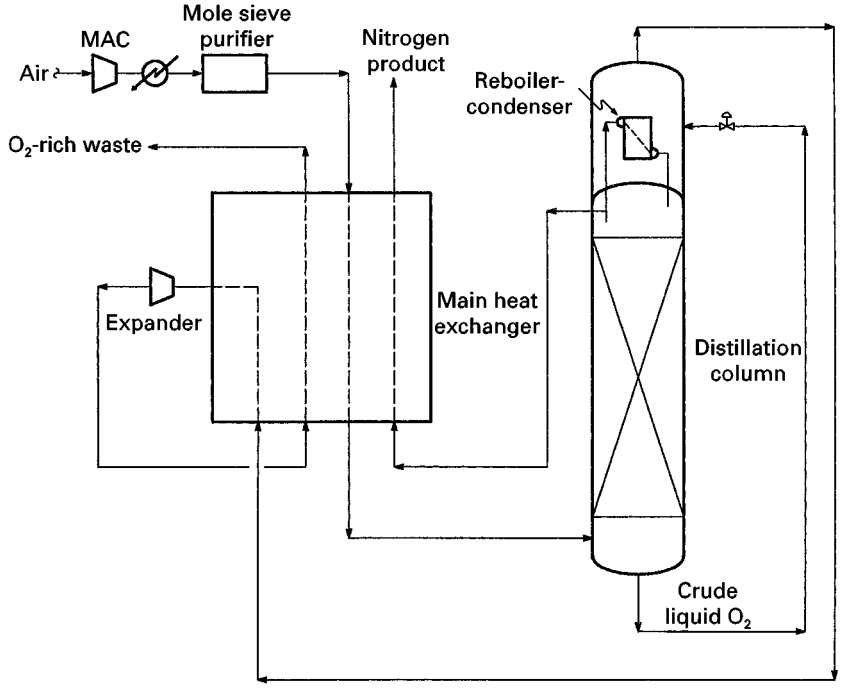

Figure 7 A single distillation column process for nitrogen production.

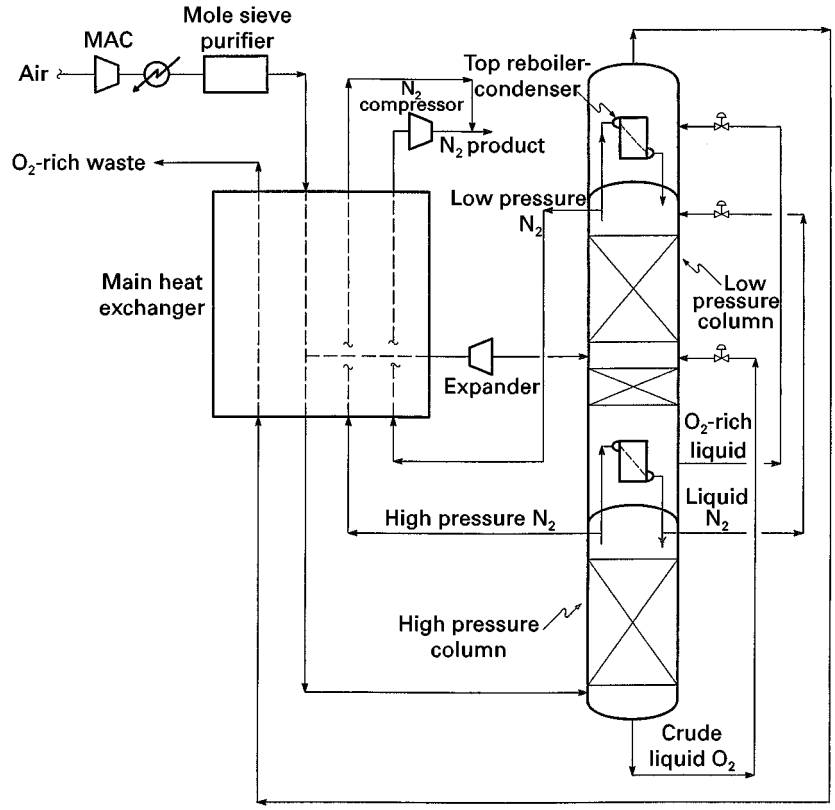

Figure 8 A two-column process fo nitrogen production.

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crude liquid oxygen from the bottom of the high pressure column is fed to an intermediate location of a low pressure column for further distillation. A low pressure nitrogen vapour stream is recovered from the top of the low pressure column as a second product stream. Another portion of this low pressure nitrogen stream is condensed in the top reboiler-condenser and returned as the major reflux stream to the top of the low pressure column. Optionally, a minor nitrogen reflux stream can also be provided to the low pressure column from the high pressure column. An oxygen-rich liquid stream containing about 70% oxygen is withdrawn from the bottom of the low pressure column, reduced in pressure and vaporized in the top reboiler-condenser. The vaporized stream is then warmed in the main heat exchanger and eventually discarded as a waste stream. Note that the refrigeration for the plant is met by expanding a portion of the gaseous feed air stream to the low pressure column in a turbo-expander. In this process, the feed air is compressed to about 8–9 atm absolute and the pressure of the low pressure column is about 3 atm absolute. A nitrogen compressor is generally used to compress the low pressure nitrogen product stream and then it is combined with the high pressure nitrogen product stream. The typical flow rate of the combined nitrogen product stream is about 72 mol per 100 mol of the feed air stream. This two-column nitrogen generator and its variations are particularly attractive for enhanced oil recovery where a very large quantity of nitrogen is injected in the wells to maintain pressure.

Ultrahigh Purity Nitrogen and Oxygen Production for the Semiconductor Industry

The fast-growing semiconductor industry uses bulk nitrogen and oxygen gases in the manufacturing of computer chips. The acceptable level of impurities in the supply of these bulk gases has been continually declining over the last decade. Currently, impurities are limited to few parts per billion (p.p.b.) and levels are expected to drop down to parts per trillion levels as wafer sizes increase. The cryogenic distillation process is the only known method of present that, in conjuction with other adsorption and catalytic processes, can meet the stringent demands of ultrahigh purity (UHP) gases.

In addition to the constituent components listed in **Table 1**, air typically consists of several impurities at p.p.m. levels. Hydrogen is a light impurity that is in the range of 1–5 p.p.m.; carbon monoxide is also present at the same levels. There are several

impurities that are heavier than oxygen – methane and higher hydrocarbons and nitrogen oxides are all present in p.p.m. concentrations. When nitrogen is distilled in one of the typical processes discussed earlier, it contains almost all the hydrogen, helium and neon and a major fraction of the carbon monoxide contained in the air. Similarly, a typical high purity oxygen contains all the unacceptable heavier impurities – krypton, xenon, methane and higher hydrocarbons, for example. Clearly the conventional distillation methods need modification to be able to supply the UHP gases.

One early method used to produce UHP nitrogen was to pass the nitrogen from a typical cryogenic distillation process over a bed of a nickel supported on silica to remove the trace levels of oxygen, hydrogen and carbon monoxide. This method is now used for back-up systems since the regular supply of UHP nitrogen is produced directly from the cold box. One distillation scheme to produce UHP nitrogen is shown in **Figure 9**.

The feed air is compressed to a pressure that is slightly greater than the pressure at which UHP nitrogen is required. This is done to supply the UHP nitrogen product directly from the cold box to the semiconductor fabrication plant without any further compression. The pressure of the supply UHP nitrogen is generally 8–10 atm absolute. The feed air after compression is heated to a temperature of about 200°C and passed over a noble metal catalyst such as platinum to oxidize all the carbon monoxide and hydrogen. The exhaust gas is then cooled and passed through the molecular sieve unit. In an alternative process, a separate noble metal catalyst is not used but instead, layers of adsorbent catalysts are supplied within the molecular sieve unit to remove hydrogen and carbon monoxide to p.p.b. level. The impurities-free air is then cooled in the main heat exchanger and distilled in a column similar to the one shown in **Figure 7**. A large number of separation stages (60–100) are used in this main distillation column to reduce the oxygen concentration in the resulting nitrogen product stream to a level of a few p.p.b.

In addition to stage count, another major difference between the processes of **Figures 7** and **9** is the manner in which crude liquid oxygen from the main distillation column is treated. In the UHP nitrogen process of **Figure 9**, crude liquid oxygen is fed to the top of a short column containing three to six stages of separation. The boil-up at the bottom of this column is provided by condensing a portion of the nitrogen vapour stream from the top of the main (high pressure) distillation column. The nitrogen and oxygen concentration in the vapour leaving the top of the short column is similar to that in air – this stream is called synthetic air. The pressure of the synthetic air is generally greater than 4 atm absolute. To recover

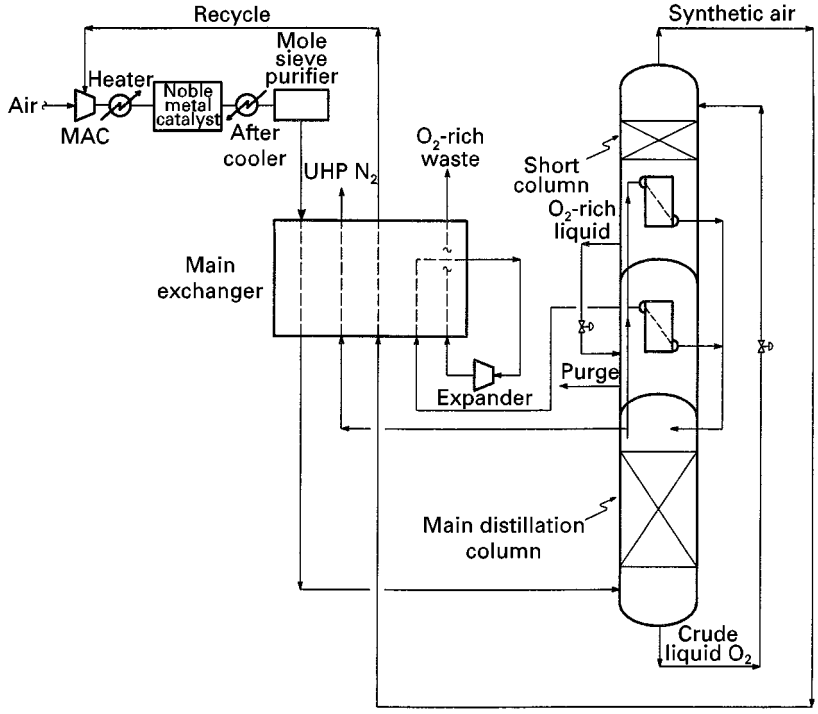

Figure 9 A UHP nitrogen scheme.

the pressure energy, this stream is recycled after further boosting its pressure to that of the main distillation column. In **Figure 9**, synthetic air is fed to an interstage of the main air compressor. This configuration saves the capital cost associated with a separate booster recycle compressor.

Not all the liquid at the bottom of the short column is vaporized; instead, an oxygen-rich liquid containing about 60–70% oxygen is withdrawn. The pressure of this liquid is reduced by 1–2 atm and then it is vaporized in a separate reboiler-condenser to produce another portion of the liquid nitrogen reflux for the main distillation column. A liquid purge stream is taken from this reboiler to prevent the accumulation of hydrocarbons to unsafe levels. The vaporized oxygen-rich stream is then expanded to provide the needed refrigeration for the plant and is eventually discharged as a waste stream.

The reason for modifying the distillation scheme of **Figure 7** to that of **Figure 9** stems from the fact that, in a UHP nitrogen process, the distillation pressure is quite high. In **Figure 7**, high pressure distillation causes the waste stream to vaporize in the reboiler-condenser at a pressure greater than 4 atm. When a large portion of the feed air (in this case 60%) is sent to the turbo-expander at such a high pressure, excess refrigeration is produced. The consequence is that the pressure energy of the waste stream is not utilized effectively and the process becomes inefficient. In constrast, the UHP nitrogen distillation scheme in **Figure 9** recovers nearly half of the crude liquid oxygen stream as a recycle synthetic air stream, thereby reducing the flow to the turbo-expander. In other words, the production of excess refrigeration is avoided and efficient operation is maintained by sending only that portion of the crude liquid oxygen stream needed for the refrigeration to the turbo-expander.

There are several other distillation schemes used for the production of UHP nitrogen. However, all the efficient schemes are based on modification of the scheme in **Figure 7**, such as is shown in **Figure 9**.

Generally, UHP oxygen is required in much smaller quantities (generally 1–5% of the UHP nitrogen production rate). It is essential that not only the concentration of a lighter impurity such as argon be in the p.p.m. to p.p.b. level but also that the concentration of heavier impurities, such as krypton, xenon and hydrocarbons, be no more than a few p.p.b. in the UHP oxygen stream. In contrast to this, a standard-grade oxygen from the process shown in Figure 4 contains about 0.5% argon and all of the heavier impurities such as methane, krypton and xenon are contained in the feed air.

A UHP oxygen distillation scheme that is a modification to the distillation configuration of Figure 9 is shown in **Figure 10**.

This modification results from an observation that, as the feed air ascends the main distillation column, all the impurities that are heavier than oxygen are rapidly reduced to nearly zero within a few separation stages. The concentration of oxygen, however, is still at significant levels. Thus, a heavies-free liquid stream is withdrawn from about 10–15 separation stages above the vapour feed air location of the main distillation column. This heavies-free liquid stream contains about 10–20% oxygen and, after pressure reduction to near atmospheric pressure, is fed to the top of the UHP oxygen column. Since the feed to this column only contains components that are more volatile than oxygen, the purpose of the column is essentially to distil off these components from oxygen. Depending on the desired purity of UHP oxygen, 60–100 separation stages are used. Since the amount of UHP oxygen to be produced is low compared to the amount of UHP nitrogen, the boil-up at the bottom of the UHP oxygen column is met by cooling crude liquid oxygen in the sump of this column. The vapour from the top of this column is typically mixed with the discharge stream from the turbo-expander. About 25% of the heavies-free liquid feed to the UHP oxygen column is recovered as UHP liquid oxygen product from the bottom of the column. It is a true credit to the cryogenic distillation industry that the stringent purity demanded by the semiconductor industry can be met without post-treatment.

DropBooks

Liquefaction

Liquid nitrogen and liquid oxygen are produced and stored in a back-up system to supply gases (after vaporization of the stored liquid) in the event of the cryogenic air separation plant shut-down. Liquid may also be supplied in tankers from a central plant location to an end-use site where the consumption of nitrogen and oxygen is not high and economically it is not justifiable to build a dedicated plant. Liquid nitrogen is also used as a source of refrigeration in such applications as food freezing.

In 1895, Carl von Linde built the first industrial-scale air liquefier. His liquefier used a Joule–Thompson (JT) valve to create refrigeration. His genius was the realization that, for the same pressure ratio across a JT valve, the amount of cooling (drop in temperature) increases rapidly as the absolute pressure of air is increased. Therefore, such a liquefier operated at about 125 atm while the pressure across the JT valve dropped to approximately 5 atm. In 1902,

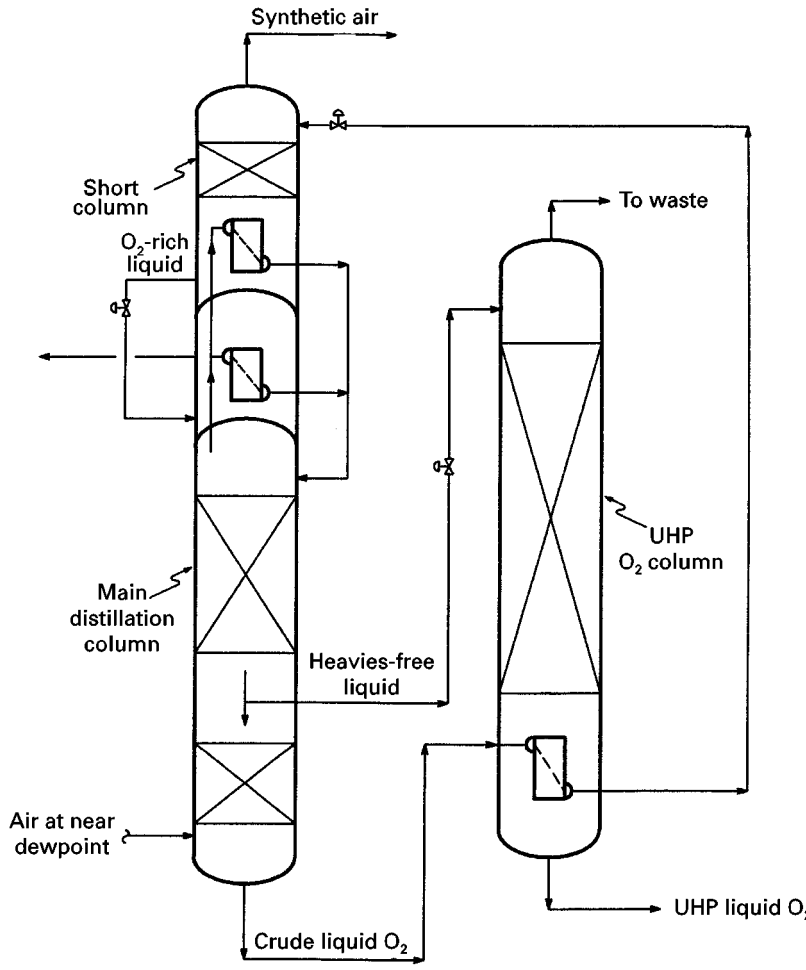

Figure 10 A distillation scheme for UHP oxygen production.

Georges Claude demonstrated that it was possible to lubricate a piston expander with petroleum ether at cryogenic temperatures. He then built an air liquefier using his piston expander. Since this liquefier did not rely on a JT valve to supply all the refrigeration, it was much more efficient than the liquefier built seven years earlier by Linde. In 1935, Kapitza built a piston expansion engine with gas lubrication and in 1939 he built an air liquefier with an expansion turbine. Most modern liquefiers use expansion turbines.

Although the early 'masters' of cryogenics were interested in liquefying air, the focus of modern liquefiers is mainly to liquefy nitrogen. This is due to the dominant use of liquid nitrogen for refrigeration supply. Liquid oxygen is generally produced by supplying some liquid nitrogen as reflux to the low pressure column of a double-column process and by withdrawing an equivalent amount of liquid oxygen from the bottom of this column. The gaseous nitrogen needed for the nitrogen liquefier is provided by any of the suitable air distillation processes described earlier. Liquefiers that are capable of producing in excess of 1000 tons per day of liquid nitrogen and oxygen are now in operation.

A two-expander nitrogen liquefier is shown in **Figure 11**.

Make-up nitrogen from an air distillation cold box is compressed to about 6 atm in a make-up compressor and is further compressed to a pressure in excess of 27 atm in a recycle compressor. The pressurized nitrogen leaving the recycle compressor is further boosted to a pressure in excess of 45 atm in compressor 1 and compressor 2, and then fed to a heat exchanger for cooling. A portion of the high pressure nitrogen stream is withdrawn near the warm end of the heat exchanger and expanded in a warm expander to provide a portion of the refrigeration needed for the liquefaction. A second portion of the high pressure nitrogen stream is withdrawn from an intermediate location of the heat exchanger and expanded in a cold expander to provide the refrigeration in the cold part of the heat exchanger. The remaining

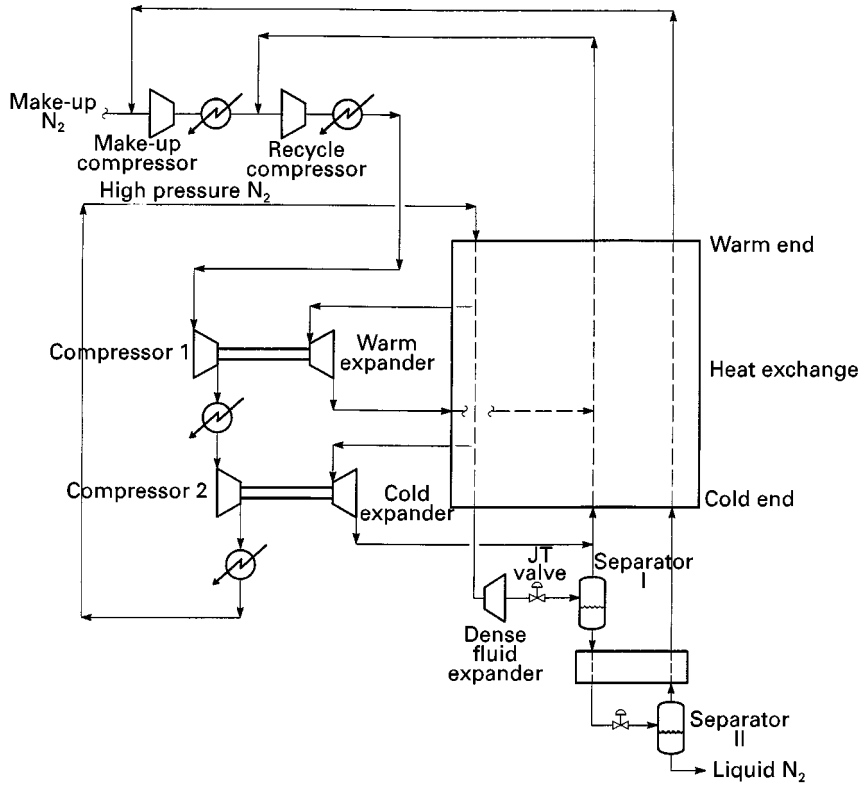

Figure 11 A nitrogen liquefier.

DropBooks

portion of the high pressure nitrogen stream exits the cold end of the heat exchanger at a temperature below $-170^{\circ}C$ and is sent to an optional dense fluid expander. The pressure drop across this dense fluid expander is maximized, subject to the constraint that very little vapour forms in the exhaust. The pressure of this stream is further reduced to about 6 atm in a JT value and the resulting two-phase stream is separated in separator I. The vapour from this separator and the exhaust streams from the cold and warm expanders are mixed at appropriate temperatures, warmed and returned to the recycle compressor. The liquid from separator I is further cooled and reduced to near atmospheric pressure through another JT valve. The resulting liquid is collected as liquid nitrogen from separator II and the vapour is recycled to the make-up compressor.

The liquefier shown in **Figure 11** is quite efficient. The use of a dense fluid expander contributes to increased efficiency but its use is optional. The working pressure range of the modern brazed plate and fin aluminium heat exchangers now approaches 100 atm. For increased efficiency, the pressure of the high pressure nitrogen steam is increased to maximum feasible values. Recently, processes using more than two gaseous expanders have been suggested for incrementally higher efficiencies.

In **Figure 11**, if none of the expanders are used then the liquefaction process reduces to the one proposed by Carl von Linde. On the other hand, if the warm expander and the dense fluid expander are removed, then the resulting process is similar to the one used by Georges Claude.

Equipment

Machinery

The selection of a compressor depends on the volumetric flow rate, the operating pressures, the compressor efficiency, its capital cost and the cost of energy. Because of their lower installation cost, centrifugal compressors are chosen over reciprocating compressors when volumetric flow rates and pressure allow their use. Axial compressors are used for large volumetric flow rates. Reciprocating machines are used at very high pressures and small volumetric flows.

For most air plants in the size range of 30–3000 tons per day of oxygen, centrifugal compressors containing three or four stages are used for compressing the feed air. Interstage cooling is provided with cooling water to approximate isothermal compression. A large fraction of the water contained in the feed air

is condensed in these interstage coolers. Most of these compressors are electrically driven; however, steam or gas turbines are occasionally used when economically justified. Air is passed through one or two stages of filtration to remove particulates prior to entry in a MAC. For plants that are larger than 3000 tons per day of oxygen, a combination of axial and centrifugal compressors is used. At the other end of the scale, for small size plants in the size range of less than 30 tons per day of oxygen, inexpensive screw compressors are used. These guidelines for oxygen plants can easily be translated to nitrogen plants, because for the same production rates, a nitrogen plant requires only 30–50% of the feed air flow required by an oxygen plant.

When gaseous oxygen is to be compressed, a centrifugal compressor is used for low to moderate pressures while a reciprocating compressor is used for higher pressures. When oxygen is needed at fairly high pressures, the initial stages of compression may be centrifugal. The design of an oxygen compressor requires careful selection of materials and seals, and total prevention of rubbing contacts to avoid ignition in the presence of high pressure oxygen. Furthermore, an oxygen compressor is generally enclosed in a building with an external barrier to increase the safety of plant personnel. Special test and start-up procedures are also used for oxygen compressors.

Expanders are used to provide refrigeration by extracting work from an expanding fluid. In the expansion process, the temperature of the expanded fluid is reduced. An air separation or a liquefaction plant generally uses a single-stage radial inflow turbine as a standard. For small plants, the work energy from the expander is either dissipated in an oil brake or through an ambient air blower. For medium to large size separation plants and liquefiers, it is essential that the work energy from an expander be recovered to increase process efficiency. This is done by either loading an expander with an electric generator or a compressor for some other process fluid. When an expander is directly coupled to a compressor, the arrangement is called a compander. As seen from **Figure 11**, companders are widely used in liquefiers. Expanders used in the cryogenic air separation and liquefaction industry typically have isentropic efficiencies in the range of 85–90%. The dense fluid expanders are essentially reverse-running liquid pumps (**Figure 11**).

Front-end Purification

The compressed air from a main air compressor must be cleaned of impurities such as water, carbon dioxide and some hydrocarbons to avoid plugging at cryogenic temperatures. The original plants used recuperative heat exchangers which were later replaced by regenerators in 1930 upon their invention by Matthias Fränkl. Around the mid-1950s, owing to the introduction of large brazed aluminium plate and fin heat exchangers, the regenerators were replaced by reversing heat exchangers. Recuperators, regenerators and reversing heat exchangers all operated to freeze the impurities within the device – complete removal of these trace components was never achieved. Beginning in the early 1980s, reversing exchangers were replaced with ambient temperature adsorption beds. Today almost all cryogenic air separation plants use molecular sieve vessels to remove impurities.

A typical two-bed adsorption system for air purification is shown in **Figure 12**. Each vessel is filled with 13X (Na-X zeolite) molecular sieve. This sieve has an excellent capacity for carbon dioxide and water removal. Sometimes an additional layer of alumina is used at the entrance for bulk water removal to decrease the energy demand during regeneration. While one bed is on stream, the other bed is being regenerated. In **Figure 12**, bed A is on stream and bed B is being regenerated. A bed is on stream for a prespecified period until carbon dioxide is about to break through the bed. At this point the feed air is directed to another bed. The pressure of the spent bed is reduced to near atmospheric pressure and a hot dry gas in the temperature range of 150–200°C is passed through the bed to desorb the adsorbed impurities. After the impurities have been removed, the bed is cooled by a flow of cool dry gas and it is then ready to be brought on

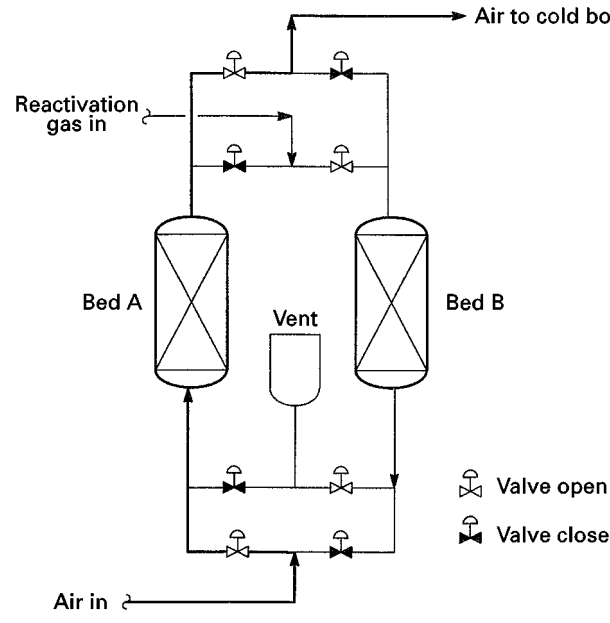

Figure 12 A front-end system for air purification.

stream. The dry gas used for regeneration is generally a portion of the gas exiting the cold box. Regeneration gas flow rate is typically in the range of 10–20% of the feed air flow. For oxygen plants, the regeneration gas is a portion of the nitrogen stream.

Heat Exchangers

Around the mid-1950s, large brazed aluminium plate and fin heat exchangers were commercially introduced. They readily became the heat exchangers of choice for cryogenic air separation and liquefaction plants. In this type of heat exchanger, corrugated fins are sandwiched between plates to form a passage for gas flow. The use of fins provides increased surface area for heat transfer. Typical fin heights range between 5 and 9 mm; fin spacing can be as low as 1 fin per mm. A heat exchanger block is formed by stacking passages. Generally, flow through individual passages is countercurrent with a warming stream in one passage and a cooling stream in the adjacent passage. A heat exchanger block can easily handle multiple warming and cooling streams. Plate and fin heat exchangers are applied in virtually all the heat exchanger services of an air separation plant. They are used as main heat exchangers, reboiler-condensers and subcoolers. The maximum size and pressure rating of these heat exchangers depend on the manufacture; however, heat exchangers 1200 mm wide by 1200 mm stack height by 6000 mm long with a pressure rating up to 50 atm can easily be found. For large size plants, multiple heat exchangers are used in parallel and careful attention is paid to the flow distribution in the manifolds.

Distillation

Until the 1980s almost all air distillation was performed in columns containing sieve trays. Due to the close relative volatility between argon and oxygen and the purity of the products, columns with over 100 separation stages are not uncommon. Therefore, tray spacing is generally 150 mm or less. Pressure drop across a large number of trays in the low pressure column increases the pressure of the boiling fluid in the low pressure column sump. This increases the pressure of the condensing nitrogen at the top of the high pressure column. In turn, the pressure of the air at the discharge of the main air compressor is increased. This leads to an increase in power consumption. As a result, there is an incentive to use a liquid–vapour contact device with lower pressure drop.

Today, most modern cryogenic air separation plants use low pressure drop structured packing in one or more of the distillation columns. The pressure drop through structured packing is only one-fifth to one-tenth that of a trayed column. The use of structured packing has led to more than 3% power savings for a typical oxygen plant. It has also allowed the use of over 175 stages of separation in the side argon column of Figure 6 for the production of argon with less than 5 p.p.m. oxygen through distillation. This eliminates the need for a second deoxidation (Deoxo) process using hydrogen and a catalyst, thereby making pure argon production much simpler.

Cold Boxes

The cryogenic equipment is enclosed in an insulated enclosure termed a cold box. A rectangular cold box consists of a steel frame with panels of sheet metal. It also provides structural support for the equipment. Cylindrical cans with insulation are also used in certain applications. Mineral wool was used for insulation prior to the late 1940s. Starting around 1948, a powdered insulation called perlite was increasingly used. The advantage of perlite is that installation costs are lower and cold boxes can be insulated with greater uniformity, leading to reduced heat leak and improved plant efficiency.

Materials of Construction

Early plants used copper or copper alloys to fabricate vessels and piping. Austenitic stainless steels were occasionally used. In the later 1950s, with the development of welding techniques for aluminium, its use became the most popular. This occurred because aluminium and aluminum alloys are easily available and are low cost and light weight. Cryogenic liquid containers are also constructed from low carbon 9% nickel steel.

Safety

Many materials react with pure oxygen, so great care is taken in the selection and clean-up of materials that come into contact with oxygen. Potential ignition sources must be minimized. All impurities that come into contact with oxygen, especially unsaturated hydrocarbons, must be reduced to safe levels. To avoid hydrocarbon build-up, generally a small purge stream is taken from the sumps where oxygen-rich liquids are being boiled. The combustion hazard increases as pure gaseous oxygen is compressed to higher pressures and therefore, special care should be taken in the compression and handling of high pressure oxygen gas.

See also: **II/Distillation:** Energy Management; Historical Development; Instrumentation Control Systems; Multicomponent Distillation; Theory of Distillation; Vapour–Liquid Equilibrium: Theory.

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AIRBORNE SAMPLES: SOLID PHASE EXTRACTION

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Introduction

Organic material in the atmosphere may exist in either the gas phase or in particles. For the purposes of this chapter, atmospheric organic material will be divided into three classes, defined by the phase distribution of the organic material in the atmosphere. Gas phase compounds will include those organic compounds which are present only in the gas phase. This will include essentially all non-aromatic organic material with fewer than about 12–14 carbon atoms. Nonvolatile organic material will include those compounds which are present in particles and whose concentrations in the gas phase are negligible compared to the particulate material. Semi-volatile organic material includes those compounds which are present in equilibrium between the gas and particulate phases in the atmosphere and for whom the concentrations in both phases are significant. The collection of gas phase and nonvolatile organic material is relatively straightforward. However, the accurate determination of the phase distribution of semi-volatile organic material requires the use of diffusion denuder technology.

Correct assessment of the contribution of fine particulate carbonaceous material to various atmospheric processes is dependent on the accurate determination and characterization of fine particulate organic material as a function of particle size. Several studies have shown that about one-third of the mass of fine particulate matter (dia. <2.5 μm) collected on filters in remote desert regions of the Southwest U.S. is organic compounds and elemental carbon. Similar fractions of carbonaceous material are found in particles collected on filters in western urban areas. In the eastern United States sulfate is the major component of filter collected airborne fine particles. However, organic material comprises one-fourth or more of the fine particulate mass. In the Northwest, organic material has been found to be the dominant fine particulate component. However, unless proper sampling procedures are used to collect particulate material, the composition of organic material in fine particles will be significantly underestimated due to losses from the semi-volatile particulate organic fraction during sample collection, i.e. a 'negative' sampling artifact.